

PARTICLES OF DIFFERENCE

Conference on Air Quality II

September 19–21, 2000; McLean, Virginia

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Conference on Air Quality II: Mercury, Trace Elements, and Particulate Matter
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Atmospheric aerosols have received increased attention over the past decade mainly for two reasons: their association with impairment of human health and their possible influences on climate change. The prospect of new regulations on fine particles, PM-2.5, particulate matter of aerodynamic diameter less than 2.5 μm , makes it mandatory that the processes governing the loading and distribution of these aerosols be sufficiently well understood to permit development of effective and efficient strategies to achieve prospective standards. Likewise, the need to relate observed climate change over the industrial period to the totality of influences makes it mandatory to identify aerosol phenomena that may substantially influence climate change and to quantify these influences. Atmospheric aerosols are also directly associated with reduction in visibility and with long-range transport and deposition of air pollutants. This talk reviews current issues and recent findings involving atmospheric aerosols and points to necessary directions of research.

The key driving force for standards for atmospheric aerosols is their association with impairment of human health. There is a large body of research adducing such an association, ranging from laboratory studies to field epidemiology and hospital admission rates. However the causative agent or agents remain unknown: Are adverse health effects due simply to mass loading, or are they associated with specific aerosol properties?

Early assessments of the climatic influence of anthropogenic aerosols due to light scattering and modification of cloud reflectance established that the cooling influence of these phenomena is comparable to the warming influence of increased concentrations of greenhouse gases and that the aerosol influences may be offsetting a considerable fraction of the warming influence of anthropogenic greenhouse gases. A major distinction is that the aerosols are relatively short-lived in the atmosphere (*ca.* 1 week) compared to the greenhouse gases (decades to centuries), so that the effect of aerosols is to mask the climate influence of greenhouse gases rather to serve as a solution to greenhouse warming. Aerosols also modify cloud lifetimes by inhibiting precipitation and by causing clouds to evaporate through absorptive heating of the atmosphere. Extinction of solar radiation by aerosol particles reduces the irradiance received at the surface, decreasing crop productivity and inhibiting evaporation, influencing the hydrological cycle.

It is no longer appropriate, if it ever was, to think of atmospheric aerosols as homogeneous spheres of uniform composition and size. Within the United States, and even more globally, not only the mass loading but also the composition, morphology, and size distribution of atmospheric aerosols are highly variable, as a function of location, and at a given location as a function of time. Particles of a given aerodynamic size may differ from one another, and even within individual particles material may be inhomogeneously distributed, as for example, carbon spherules imbedded in much larger sulfate particles. Some of the particulate matter is primary, that is, introduced into the atmosphere directly as particles, such as carbon particles in diesel exhaust. Some is secondary, that is, formed in the atmosphere by gas to particle conversion. Much of the material is inorganic, mainly sulfates and nitrates resulting mainly from energy-related emissions. Some of the material is carbonaceous, in part primary, in part secondary, and of this material some is anthropogenic and some biogenic.

While the heterogeneity of atmospheric aerosols complicates the problem of understanding their loading and distribution, it may well be the key to its solution. By detailed examination of the materials comprising aerosols it is possible to infer the sources of these materials. It may be possible as well to identify specific health impairing agents. The heterogeneity of aerosol particles is thus the key to identifying their sources, to understanding the processes that govern their loading and properties, and to devising control strategies that are both effective and efficient. Future research must therefore take cognizance of differences among aerosol particles and use these differences to advantage.

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Tropospheric aerosols are of current regulatory and scientific concern principally because of their association with impairment of human health and possible influences on climate change. Atmospheric aerosols are also directly associated with visibility reduction, with long-range transport and deposition of air pollutants, and with influences on atmospheric chemical processes. The prospect of new regulations on particulate matter of aerodynamic diameter less than 2.5 μm , makes it mandatory that the processes governing the loading and distribution of these aerosols be sufficiently well understood to permit development of effective and efficient strategies to achieve prospective standards. Aerosol particles are highly heterogeneous, from location to location, from time to time at a given location, as a function of size at a given time and location, and from particle to particle within a given size fraction. Thus aerosols must be considered a complex of substances not a single substance. This situation makes it clear that no single control strategy will be effective in reducing aerosol loading and that effective control strategies must be tailored to specific locations. Development of such tailored control strategies must rely on understanding of the processes governing the loading of aerosols as represented in models and as demonstrated by comparison with observations. Many new techniques are available to provide the needed understanding of aerosol properties and processes, but acquiring this understanding will require a substantial commitment of effort and resources.

INTRODUCTION

An aerosol is a two-phase (or higher) system consisting of small solid and/or liquid particles suspended in air. Atmospheric aerosols include dust, haze, smoke, smog, all of which are manifested by scattering of visible radiation. Tropospheric aerosols are of concern principally because of their association with impairment of human health and influences on climate change by modifying the radiation budget and the properties of clouds. Atmospheric aerosols reduce visibility, contribute to long-range transport and deposition of air pollutants, and exert chemical and radiative influences on atmospheric chemical processes. Tropospheric aerosols range in size from a few nanometers to a few tens of micrometers, diameter, but the principal size range of concern is below 1 μm . New air-quality regulations under consideration in the United States would govern the loading of particles of aerodynamic diameter less than 2.5 μm (PM-2.5 standard; EPA, 1998).

Two years ago at the first conference in this series Secretary of Energy Bill Richardson reiterated the Federal Government's commitment to clean air and to the research and technology development required to achieve this goal. Very presciently with respect to the PM-2.5 issue Secretary Richardson stated:

We need to know much more than we know today about the "fingerprints" of these particles--what comes out of the stack, what comes from other sectors of our industry,

what kind of transformations occur in the atmosphere--most importantly, what sources are the biggest problems. (Richardson, 1998).

That requirement of enhanced understanding of these atmospheric issues remains with us. Fortunately many of the techniques required to address these issues are at hand.

Implicit in the promulgation of any air-quality standard is the development and imposition of regulations to meet that standard. For primary pollutants, that is pollutants which are directly emitted, such as sulfur dioxide, ambient concentrations may be straightforwardly and confidently related to emissions, and it is thus possible to develop efficient and effective strategies to meet air quality standards. In the case of secondary air pollutants, that is, those which are created by reactions in the atmosphere, such as ozone, the relation between emissions and concentrations is more complex. This situation holds all the more for atmospheric aerosols, which have both primary and secondary components, both of which derive from numerous sources, and which exhibit wide variations in their properties. It is thus a challenging task of the atmospheric chemistry research community to develop sufficient understanding of the governing processes to permit strategies to be developed to effectively and efficiently meet prospective air quality regulations.

Figure 1 shows the annual average mass-loading and composition of sub 2.5- μm aerosol at several urban locations in the United States. Average mass loading is comparable to or in excess of the proposed annual standard, 15 $\mu\text{g m}^{-3}$. More significant is the fact that the composition of these aerosols differs substantially from location to location. For example sulfate is a dominant component in the eastern part of the country, whereas it is a minor component in the west. Prior imposition of stringent controls of sulfur emissions in southern California together with the absence of import of this material from other locations makes sulfate a minor component of the aerosol there. Observations such as these make it clear that no single approach will be effective in meeting air quality standards for aerosols.

In addition to their influence on air quality, aerosols exert substantial influence on important geophysical processes. By decreasing the amount of the sun's energy that is absorbed by the planet, fine particles exert a cooling influence on climate. By serving as the particles on which cloud droplets form, aerosol particles have a direct influence on the earth's hydrological cycle. The enhanced atmospheric burdens of aerosols as a consequence of industrial emissions is thought to suppress precipitation and to enhance residence time of clouds, with resultant radiative effects (Rosenfeld, 2000). Alteration of these processes by anthropogenic aerosols is thought to have exerted a significant change on the earth radiative balance and on the distribution of the deposition of solar energy between the atmosphere and the Earth's surface. The magnitude of the overall cooling influence is uncertain by at least a factor of two, but all recent estimates (e.g., IPCC, 1996; Haywood, et al., 1999) indicate that it is comparable to the warming influence of increased concentrations of greenhouse gases and may consequently be offsetting a major fraction of the greenhouse warming that would otherwise have been experienced over the industrial period. A major distinction is that the aerosols are relatively short-lived in the atmosphere (*ca.* 1 week) compared to the greenhouse gases (decades to centuries), so that the effect of aerosols is to mask the climate influence of greenhouse gases rather to serve as a solution to greenhouse warming.

Understanding of aerosol processes required for developing air quality standards and strategies to meet them is required also for developing approaches to dealing with the climate

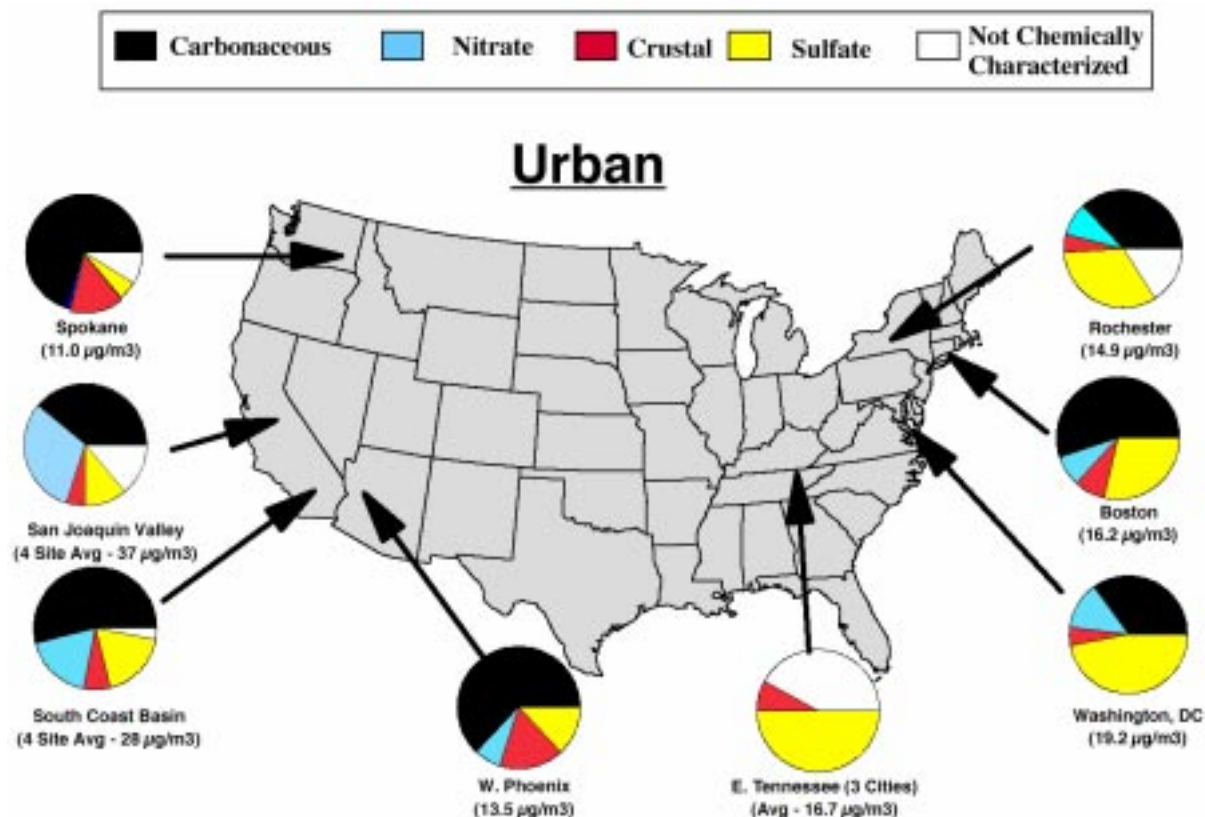


Figure 1. Annual average mass-loading and composition of sub 2.5- μm (aerodynamic diameter) aerosol based on at least one year of monitoring at two or more sites in the same region. As data were obtained using a variety of methods, these concentrations should not be used to determine compliance with the proposed PM-2.5 standard. From EPA (1998).

change issue. Because the aerosol offset to the warming influence of enhanced concentrations of CO_2 and other greenhouse gases is not well known, it is not possible to confidently relate observed climate change to increased concentrations of greenhouse gases nor to confidently develop targets for prospective greenhouse gas concentrations.

Understanding of aerosol processes required for developing air quality standards and strategies to meet them is required also for developing approaches to dealing with the climate change issue. Because the aerosol offset to the warming influence of enhanced concentrations of CO_2 and other greenhouse gases is not well known, it is not possible to confidently relate observed climate change to increased concentrations of greenhouse gases nor to confidently develop targets for prospective greenhouse gas concentrations.

This paper reviews present understanding of aerosol properties and processes with an aim toward identifying research that is necessary to developing and demonstrating model-based understanding that is required for making effective and efficient policy regarding tropospheric aerosols and for achieving standards in fulfillment of this policy.

THE DISTRIBUTION OF TROPOSPHERIC AEROSOLS

The prime consideration in any examination of tropospheric aerosols is their geographical distribution. Much progress has been made in recent years in characterizing this distribution on a variety of scales. Figure 2 shows an example of the global distribution of aerosols determined by satellite measurement of aerosol radiance; the technique is suitable only over homogeneous dark surfaces, that is large water bodies. Although the satellite measurements provide daily global coverage, the requirement of rigorous exclusion of clouds results in rather sparse data recovery, so observations are typically pooled for a period such as one month. The radiance due to aerosols is converted by a model into aerosol optical depth, albeit with considerable uncertainty. (Optical depth, τ , characterizes the transmittance of light by the aerosol, such that the fractional transmittance of direct radiation is given by $\exp -\tau$.) Major patterns in aerosol optical depth can be readily discerned in the figure: dust plumes off of deserts, plumes associated with biomass burning in the tropics, and plumes of industrial aerosol from North America, Europe, and Asia. Note the much greater aerosol loading in the midlatitudes of the Northern Hemisphere than the Southern, which is much less influenced by industrial activities. An important recent development is the ability to infer information about the size of the aerosol from satellite measurements. The lower panel of Figure 2 shows the Ångström exponent α , the negative of the slope of optical depth versus wavelength on a double logarithmic plot. The smaller the particle, the stronger the wavelength dependence of light scattering, and hence the greater the Ångström exponent. This representation of the data readily distinguishes the larger particles in the dust plumes (typically greater than 1 μm diameter) from the much smaller particles in the plumes extending from industrial regions.

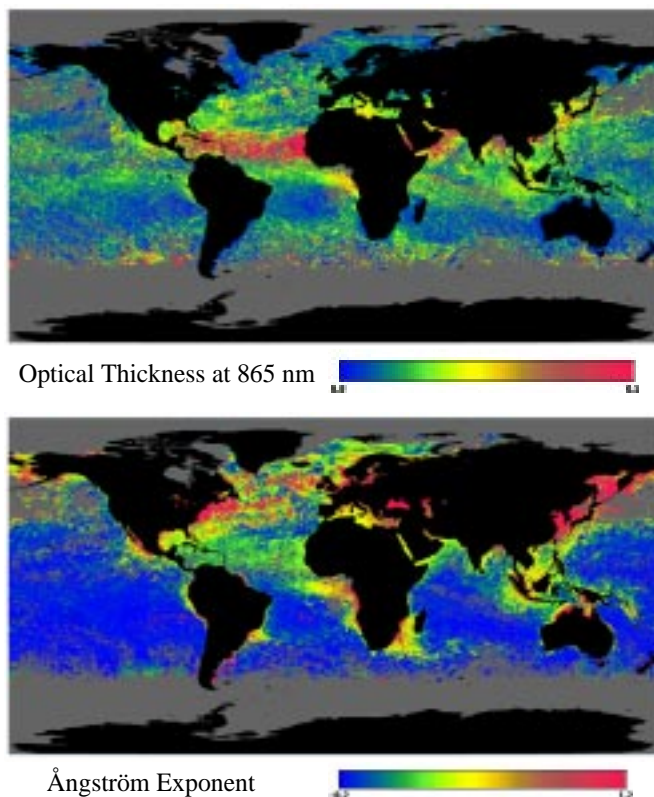


Figure 2. Global distribution of aerosol optical thickness τ at 865 nm (upper panel) and dependence on wavelength λ as the Ångström exponent, $\alpha = -d \ln \tau / d \ln \lambda$, (lower panel) for June 1997 at 18-km resolution, derived from radiance measurements by the POLDER (POLarization and Directionality of the Earth's Reflectance) radiometer aboard the ADEOS (ADvanced Earth Observing Satellite) platform. Retrieval is limited to water surfaces. Courtesy of Laboratoire d'Optique Atmosphérique, Lille, France; Laboratoire des Sciences du Climat et de l'Environnement, Gif sur Yvette, France; Centre National d'études Spatiales, Toulouse, France; and National Space Development Agency, Japan. For further information see <http://earth-sciences.cnes.fr:8060/polder/Mission.html>.

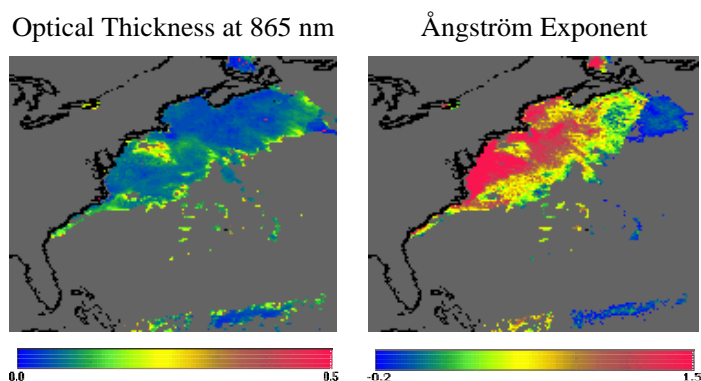


Figure 3. Distribution of aerosol optical thickness at 865 nm (left) and Ångström exponent (right) off the eastern seaboard of the United States for a single satellite overpass on April 16 1997, as in Figure 2.

Satellite-based measurements such as these can also yield instantaneous distributions. Figure 3 shows examples of such measurements from a single satellite overpass. Although the data recovery is sparse because of cloud interference, the figure brings out the pattern of aerosols leaving the eastern seaboard of the U.S. as well as possible evolution in properties as a function of distance from the coast.

Satellite based techniques are being extended to infer aerosol absorption as well as optical depth (Nakajima *et al.*, 1999) and to permit characterization over land surfaces. Such measurements are proving invaluable in examination of the sources and transport of aerosols.

A complementary characterization of aerosol loading is the time series at a given location. Aerosol optical depth and Ångström exponent may be accurately determined by sunphotometry from the surface. Figure 4 shows a time series of these quantities at a rural location in the central United States; obtaining such a data set requires considerable commitment of effort and attention to detail. Several important features may be discerned from these data. First attention is called to the annual cycle, greater optical depth in the summer than in the winter. This is due

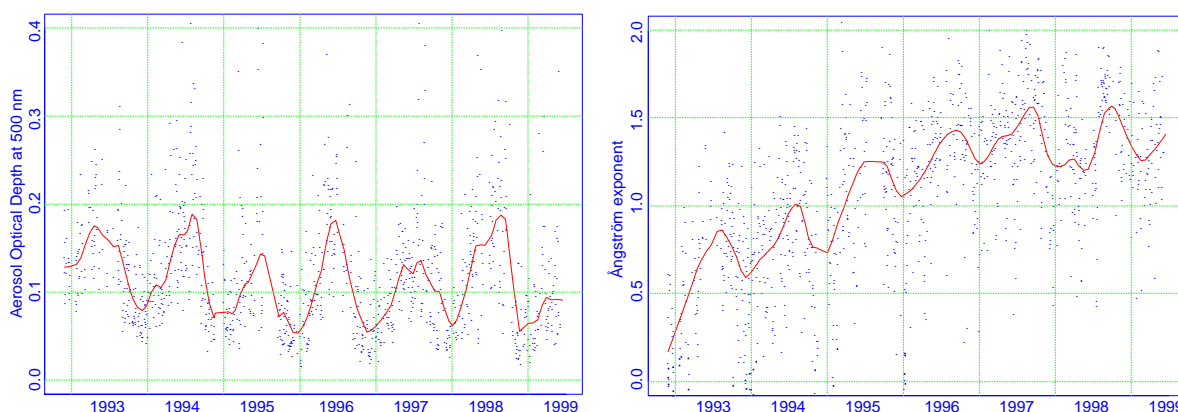


Figure 4. Time series of aerosol optical depth (left) and Angstrom exponent (right) at Department of Energy Atmospheric Radiation Measurement site in North Central Oklahoma over period 1993 to 1999. Measurements are by sun photometry. Points represent daily average; red curve is smooth fit of data to guide the eye. (Courtesy of J. Michalsky, Pacific Northwest National Laboratory).

mainly to enhanced atmospheric production of secondary aerosol in summer. The annual cycle is reflected also in particle size, with smaller particles in summer, indicative of a greater fraction of the aerosol particles being due to atmospheric production and/or to a shift of these secondary particles to a smaller size distribution. A second important feature is the decreasing trend in optical depth in the early years of the record, especially noticeable in winter. This is due the slow decrease in *stratospheric* aerosol resulting from the eruption of Mount Pinatubo in the Philippines in 1992; concurrent with this decrease in loading is a gradual increase in Ångström exponent, corresponding to an decrease in particle size, again representing the decreasing contribution of stratospheric aerosol to the total signal. A third important feature is the very large day-to-day variability of both quantities. This variation, which is due almost entirely to variation in the loading and properties of *tropospheric* aerosol, illustrates the control of the aerosol loading by the governing mesoscale meteorology, that is the meteorological scale that is responsible for day-to-day changes in weather, which governs aerosol formation, transport, and removal. Unfortunately the data base of such measurements is rather limited, but attention is called to a worldwide network spearheaded by investigators at NASA (Holben *et al.*, 1998).

The vertical distribution of aerosols is also important, especially with respect to their hydrological and radiative influences. This distribution can be measured continuously by Lidar (Laser radar). Figure 5 shows an example over a 24-hour period. The rapid evolution of the aerosol loading and vertical distribution should be noted. Generally the greatest aerosol concentration is within two kilometers of the surface, a consequence of the surface source, relatively short atmospheric residence time, and removal associated with cloud formation and precipitation. However frequently the maximum concentration is well above the surface, and often the aerosol aloft is decoupled from the aerosol at the surface. Characterization of aerosol vertical and geographical distribution by satellite-borne lidar has also been demonstrated. A lidar deployed on the space shuttle in 1994 returned detailed pictures of the vertical distribution of aerosols along the course of the satellite (JPL, undated; Strawbridge and Hoff, 1996) and served as a testbed for an instrument planned for launch in 2003, which will provide distributions of aerosol extinction, optical depth, and single scattering albedo (NASA, undated).

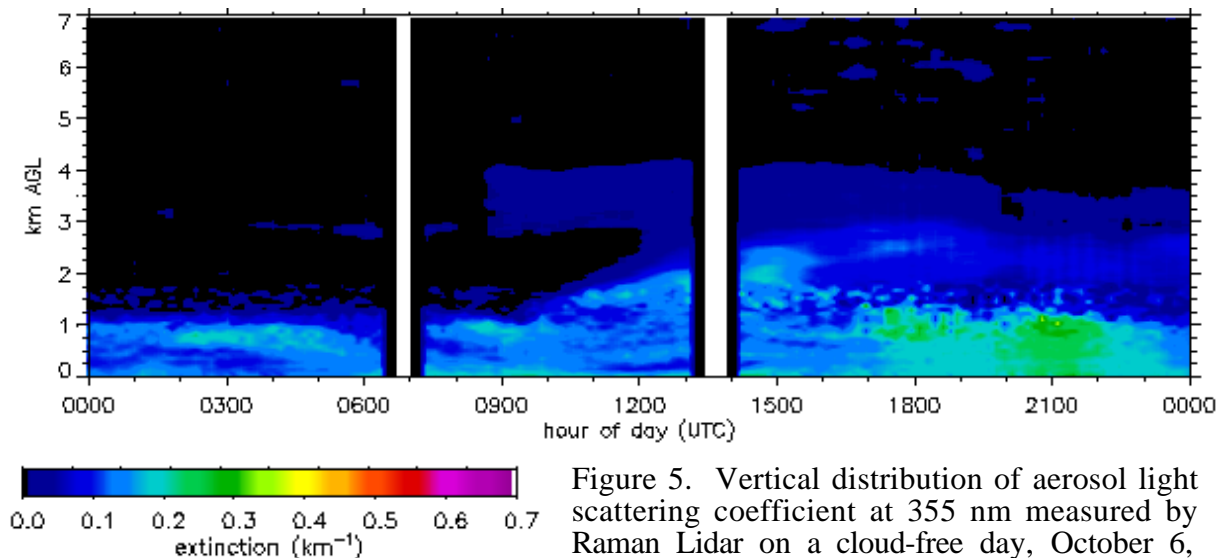


Figure 5. Vertical distribution of aerosol light scattering coefficient at 355 nm measured by Raman Lidar on a cloud-free day, October 6, 1999, at Department of Energy Atmospheric Radiation Measurement site in North Central Oklahoma. (Courtesy of D. Turner, Pacific Northwest National Laboratory).

PHYSICAL CHARACTERIZATION

Although remote sensing provides a good picture of the areal or vertical distribution of aerosols, it cannot provide any detailed characterization of aerosol physical or chemical properties needed to identify the sources of the aerosol material and to determine its influence on the several issues of concern, for which *in-situ* measurements are required. Much *in-situ* characterization is based on aerosol physical properties, which can often be rapidly determined, permitting continuous, high-frequency measurements. A key variable is the particle size distribution as light scattering, cloud nucleating ability, and penetration into airways of the lung are all dependent on particle size. Particle size can be measured continuously by mobility analysis over the range 0.003 to 0.6 μm . Figure 6 consists of a series of successive scans that are composited to form a continuous record. The figure shows a rather rare occurrence of a burst of ultrafine particles that is attributed to a recent nucleation event, though it must be recognized that particles must be several hours old to have grown from nucleation threshold (diameter at which accretion of new mass becomes thermodynamically favored) to the size, 3 nm, at which they can be detected. Information such as this is essential in interpreting the processes responsible for the loading and properties of the aerosol.

Light scattering coefficient is another important physical property of aerosols that can be measured with high frequency, Figure 7. Here the light scattering coefficient is that of the dried aerosol so the signal is not affected by relative-humidity (RH) dependent growth of the aerosol. The time series over the month indicates some low-frequency events such as the decrease in aerosol loading on January 23 that was evidently associated with frontal passage. However there is much high-frequency information evident as well, in particular the consistent occurrence of a diurnal cycle (daytime maximum) indicative of a substantial photochemical component. Such information is lost in daily averages, indicated in the figure or, even worse, in 6-day averages of the mass.

Much aerosol material consists of substances that are hygroscopic (taking up water with increasing relative humidity) or deliquescent (undergoing solid-to-liquid phase transition associated with water uptake). This water uptake, which depends mainly on composition,

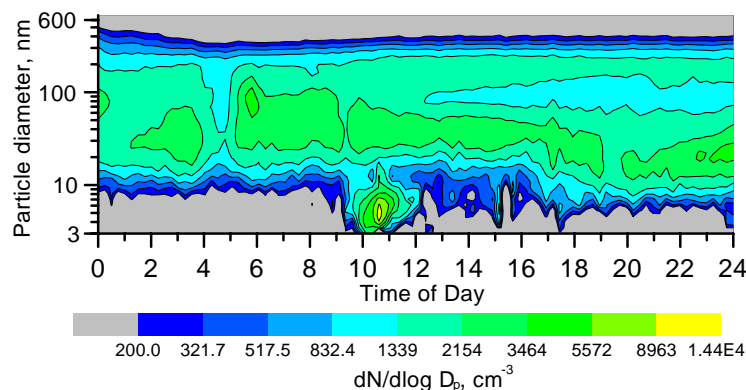


Figure 6. Time series of the size distribution of particles at Hohenpeissenberg, Germany, a rural, partially forested site, ca. 1000 m elevation, on May 16, 1999, determined by mobility analysis. Each individual mobility scan requires 10 minutes. Gray area denotes concentration below 200 particles per cm^3 per logarithm of diameter. Note burst of nucleation-mode particles in mid morning. (Courtesy of W. Birmili, Institut für Troposphärenforschung, Leipzig).

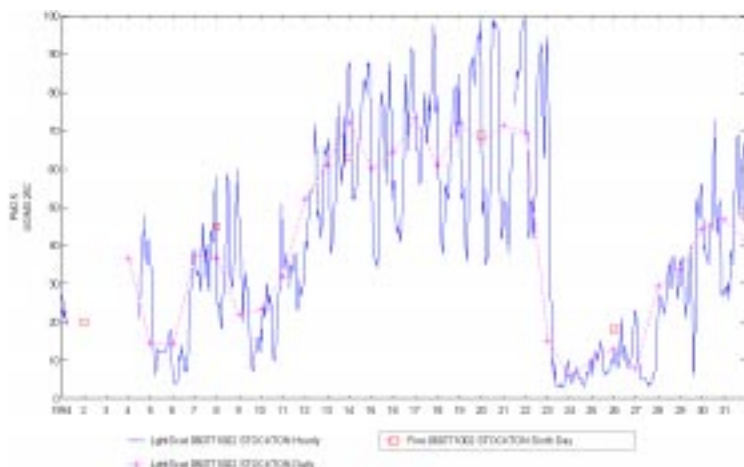


Figure 7. Time series of light scattering coefficient and fine particle mass in Stockton CA over the month of January, 1994. Light scattering coefficient is scaled to fine particle mass by daily averages. From Husar (1997).

greatly influences particle size and associated physical properties and in turn aerosol effects such as penetration into airways of the lung and radiative forcing of climate. Figure 8 shows the results of laboratory studies of the influence of relative humidity on the uptake of water by aerosols. Figure 8a shows the influence of relative humidity on composition for a single substance, ammonium sulfate; figure 8b shows the influence of RH-dependent growth on light-scattering coefficient of key inorganic aerosol components. Such studies make it clear that composition plays a major role in RH-dependent growth, offering yet a further reason that aerosol composition must be characterized. In contrast to these hygroscopic substances, non-hygroscopic materials exhibit essentially no growth with increasing relative humidity.

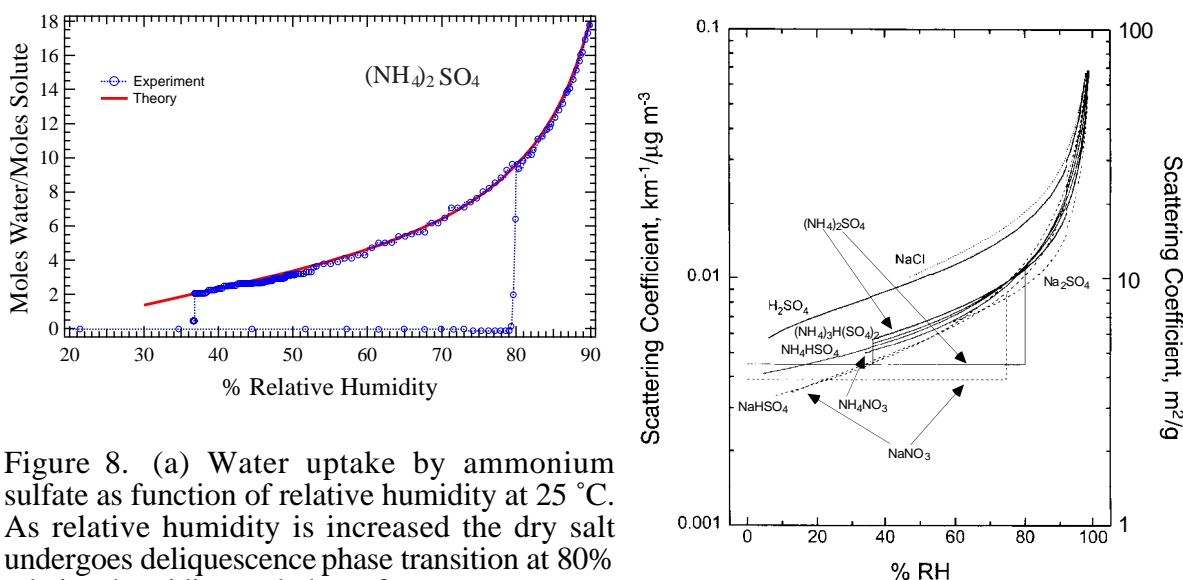
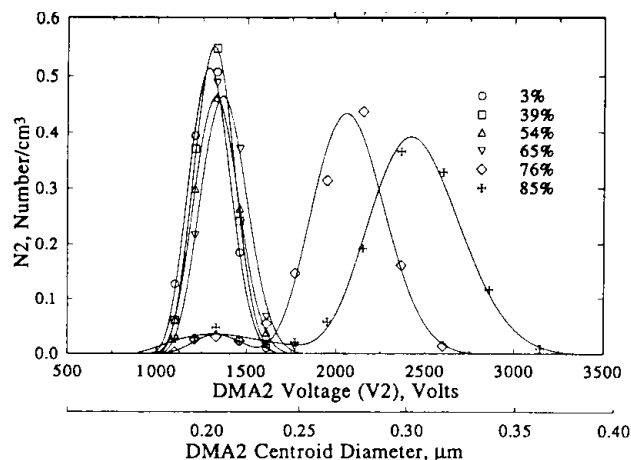


Figure 8. (a) Water uptake by ammonium sulfate as function of relative humidity at 25 °C. As relative humidity is increased the dry salt undergoes deliquescence phase transition at 80% relative humidity and thereafter accretes water

continuously. As relative humidity is decreased below the deliquescence point the particle retains water until the efflorescence point is reached, 37% relative humidity. (Courtesy of T. Onasch, Brookhaven National Laboratory). (b) Comparison of relative humidity dependence of light scattering coefficient of several inorganic salts and acids present in atmospheric aerosols. Deliquescence transitions are noted for several species. Efflorescence, if it occurs, generally occurs at much lower relative humidity. For these calculations dry particle size distribution was taken as lognormal with geometric mean diameter 0.3 µm and geometric standard deviation 1.5. (Tang, 1996).

Figure 9. Differential mobility scan of particle size. Aerosol was passed through a mobility analyzer at low relative humidity (5-25%) set to transmit particles with diameter centered about 0.2 μm . The exiting airstream was then passed through a second mobility analyzer, which was scanned at the indicated relative humidities. Measurements at Hopi Point, Grand Canyon, Arizona, March 1, 1990, 14:15. From Zhang *et al.*, 1993.

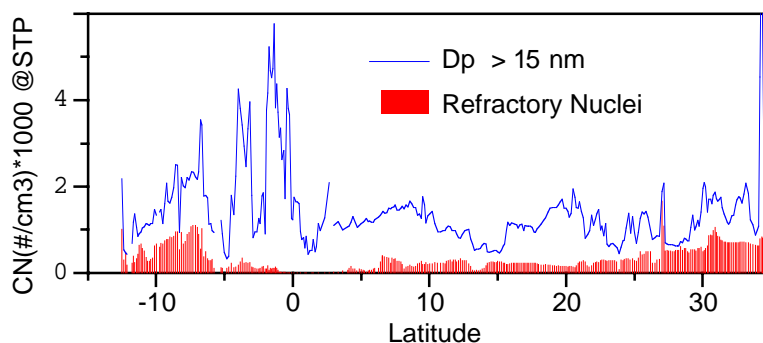


The dependence of particle size on relative humidity has stimulated the development of techniques to characterize particles by their RH-dependent growth. An example of such measurements is shown in Figure 9. Two mobility analyzers are operated in tandem. The first analyzer is operated at a low relative humidity (here 5-25%) and is set to transmit particles centered about a specific diameter, here 0.2 μm . The RH in the second mobility analyzer is increased in successive scans. For RH up to 65% the aerosol size was essentially unchanged. At RH 76% and 85% most particles had deliquesced and had grown to the larger diameters indicated. A small but significant fraction of particles exhibited no RH-induced growth. The situation of the particles of a given dry diameter exhibiting less- and more-hygroscopic components is widespread. Findings such as these demonstrate that particles of a given dry size exhibit different compositions, from which one infers that the particles have different sources and history in the atmosphere.

Other aerosol characterization techniques use the differential volatility of different aerosol substances to draw inferences about chemical composition. Figure 10 shows traces of the concentration of aerosol particles before and after heating to 300°C to drive off volatile material. This analysis demonstrates that an appreciable and variable fraction of the particles sampled during a flight over the tropical western Pacific Ocean at an altitude of 8 km had formed on surface-derived nonvolatile cores characteristic of soot, seasalt, or dust and at the same time that there are instances in which the aerosol is dominated by particles that have no nonvolatile core, consistent with homogeneous nucleation processes in the atmosphere.

Figure 10. Time series of number concentrations of particles having diameters greater than 15 μm and of particles having nonvolatile refractory cores after being heated to 300°C. Measurements were made near 8 km over the western Pacific on a flight from Darwin to Tokyo on June 1, 1990, as part of the NASA GLOBE mission.

(Courtesy of V. Kaspustin and A. Clarke, University of Hawaii; see http://pali.soest.hawaii.edu/projects/nasagiss_p3.html).



CHEMICAL CHARACTERIZATION

For all the insights that may be obtained from physical characterization of aerosols, the greatest insight into their sources comes from chemical analysis. Chemical composition may well also be the key to understanding the mechanism of health impairment by aerosols. Traditionally determination of composition has consisted of sample collection by filtration, or, for size resolved analysis, by multi-stage impactor, followed by dissolution and chemical analysis. This approach has been applied to both the inorganic and organic components. Figure 11 gives an example of such data. In addition to the increased concentrations at the downwind site, the enhancement of specific components is evident, particularly nitrate, ammonium, and organics. Data such as these immediately suggest the aerosol components on which to focus attention. Size dependent composition has implications on inhalation and also on light scattering and its dependence on relative humidity.

An important recent development is real-time sampling and analysis of soluble inorganic aerosol species. This technique subjects ambient air from which super 2.5 μm particles have been removed by impaction and gaseous HNO_3 and NH_3 have been removed by denuder to a high supersaturation that effectively converts aerosol particles into cloud droplets, which are collected and analyzed by ion chromatography. Figure 12 shows the time series of concentrations of major aerosol species determined by this method over a 10-day period in Atlanta, Ga. Note the large sub-daily variation of the several component species as well as the total sub-2.5 μm mass. Sulfate was a major component of the mass, but its fractional contribution varied substantially, comprising a much smaller fraction in the early period of the record than later. Nitrate, a small fraction of the total mass, exhibited much more rapid fluctuation than sulfate or total mass, with frequent peaks in midmorning, perhaps indicative of a local photochemical source. Sulfate, exhibiting slower fluctuations, evidently arises from more widespread sources. Panel *c* compares the equivalents of anions sulfate and nitrate with ammonium. In all instances the sum of nitrate plus sulfate exceeded ammonium; the difference, ascribed to hydrogen ion, is indicative of a several-day episode of quite acidic aerosol. All information of the different time dependences of the several species, with resulting inferences regarding sources, as well as possible implications on health effects, is lost in conventional 24-hour filter sampling and analysis. Worse still, of course, is the widespread practice in the United States of taking one 24-hour sample every sixth day.

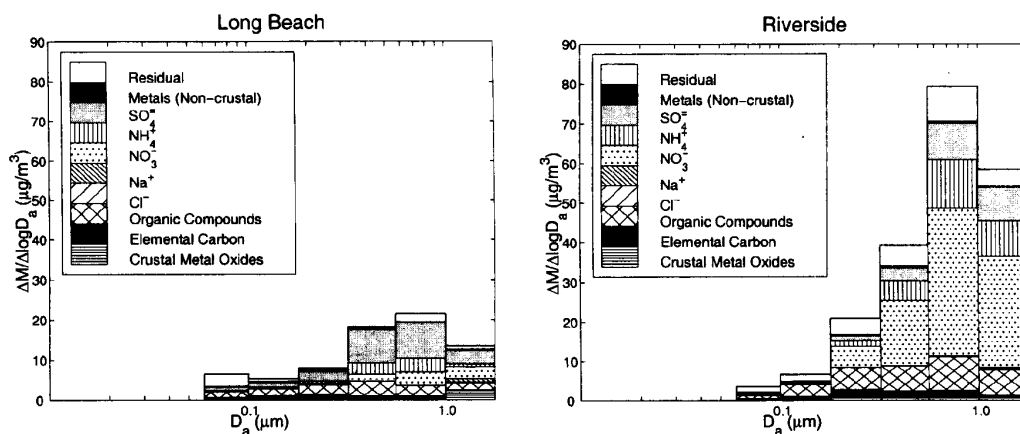
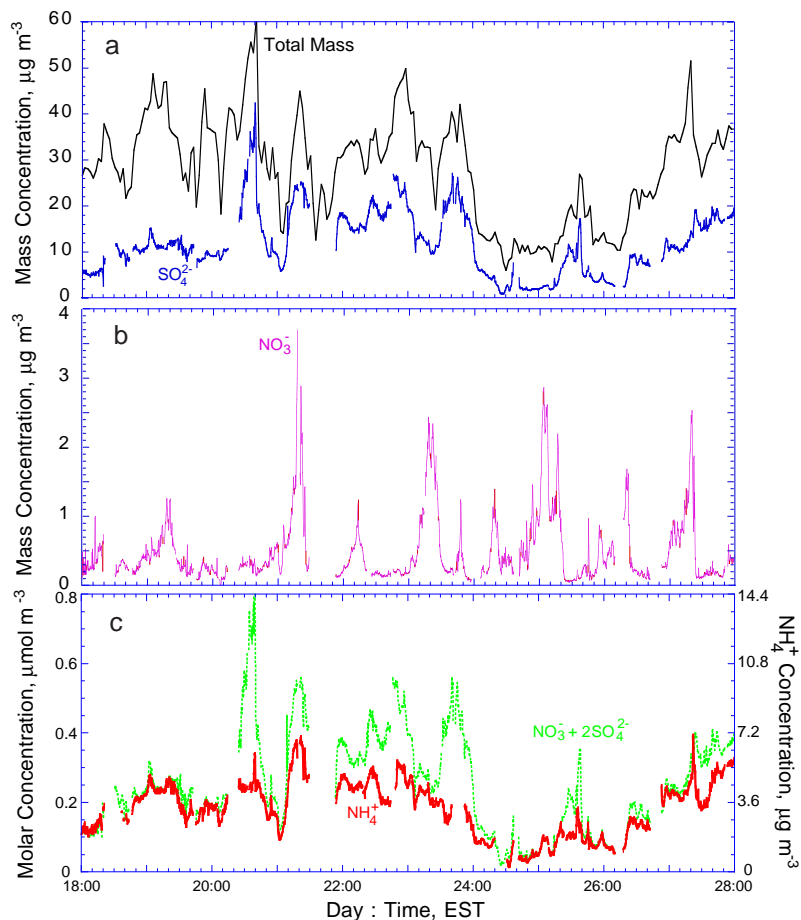


Figure 11. Size segregated aerosol composition at two sites upwind (Long Beach) and downwind (Riverside) of major aerosol sources in Los Angeles. Samples represent composites of several 4-hour samples taken on different days. From Hughes *et al.* (1999).

Figure 12. Time series of (a) sub-2.5 μm aerosol mass concentration determined by Tapered Element Oscillating Microbalance and of the concentrations of sub-2.5 μm (a) sulfate, (b) nitrate, and (c) ammonium, determined at 7-minute time resolution by condensational growth and impaction of ambient aerosol followed by ion-chromatographic analysis. Also shown (c) is the total equivalents of nitrate and sulfate. Measurements were made at an urban site in Atlanta, Ga., August 18-28, 1999. (Courtesy of Y.-N. Lee, Brookhaven National Laboratory and R. Weber, Georgia Institute of Technology).



Key among the new techniques is single-particle mass spectrometry. Studies within the past several years have used time-of-flight mass spectrometry to examine the composition of multiple species within individual aerosol particles. Particles are ablated by a laser beam, producing positive and negative ions, which are analyzed in the mass spectrometer; particle sizes are calculated from their velocities. The resulting spectrum gives a semi-quantitative picture of the composition of the individual particles. Examples of such spectra are given in Figure 13. The particles in panels *b* and *c* though similar in size have discernibly different composition. It is not yet possible to quantitatively infer composition from the mass spectra; ion currents exhibit nonlinear dependence on laser power and particle size, and there are interactions among the substances present that greatly influence the magnitudes of the ion currents. Nonetheless it is possible to distinguish different types of aerosol particles at a given location and time, even within the same size range, and to draw conclusions about the numbers of different types of particles and their state of internal mixing.

Transmission electron microscopy provides exquisitely detailed information on the composition of single particles; Figure 14 shows an example. Buseck and his colleagues have found that the great majority of sulfate aerosol particles contain soot inclusions in samples collected above the North Atlantic ocean during a pollution episode and that even in the clean atmosphere above the Southern Ocean up to half of the sulfate particles contain soot (Buseck and Pósfai, 1999).

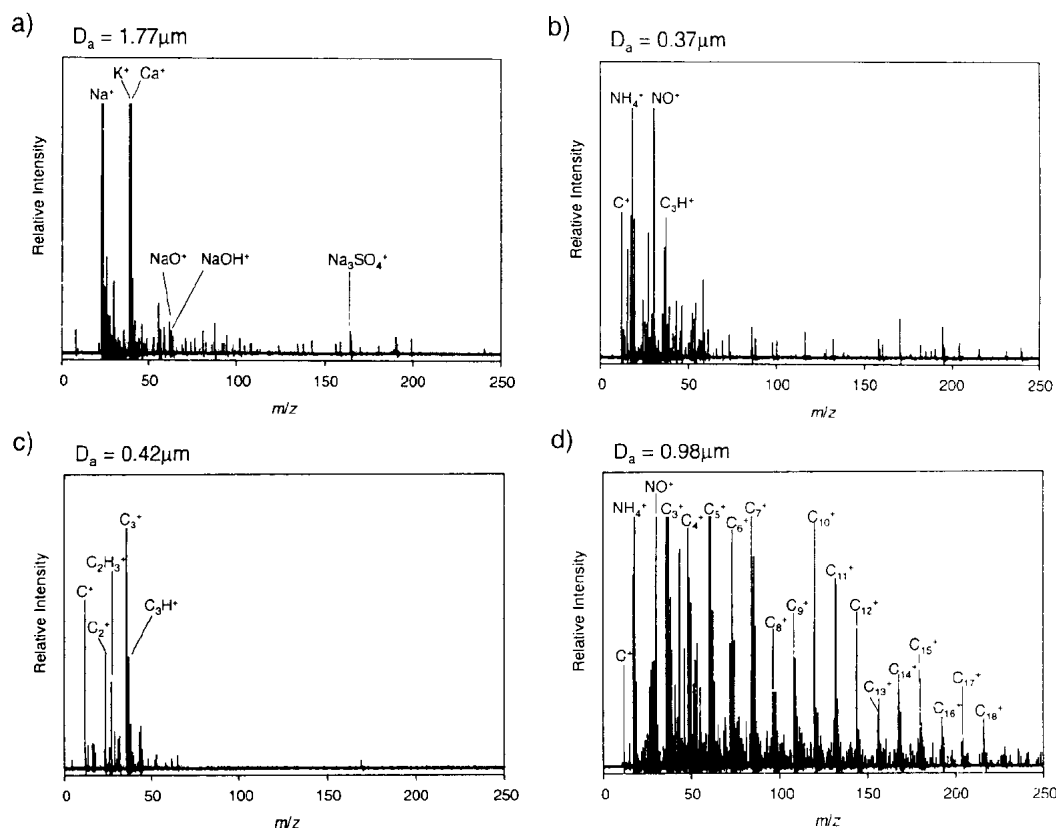


Figure 13. Examples of mass spectra of individual aerosol particles sampled in the vicinity of Los Angeles. (a) Sea salt particle; (b) ammonium nitrate-containing particle with organic carbon inclusions; (c) organic carbon particle; (d) predominantly elemental carbon particle with some ammonium nitrate content. From Hughes *et al.* (1999).

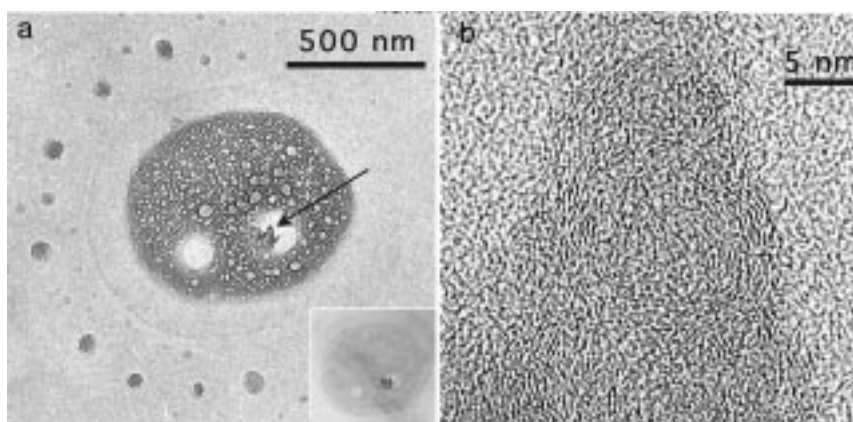


Figure 14. Transmission Electron Microscopy (TEM) images of a single particle consisting mainly of $(\text{NH}_4)_2\text{SO}_4$ with a soot inclusion. Rings of small $(\text{NH}_4)_2\text{SO}_4$ crystals and halos in (a) formed as the sulfate particle dehydrated within the TEM. The presence and dimensions of such halos can be used to distinguish among particles that likely had different water contents while airborne. The arrow points to a soot aggregate, a portion of which is shown in high resolution in (b). Sample was obtained in an unpolluted air mass in the vicinity of Tasmania. From Buseck and Pósfai (1999).

CHARACTERIZING EMISSIONS

Characterization of the nature and magnitude of sources of primary aerosols is a major issue facing the scientific and regulatory communities. As should be clear from the discussion above this characterization must go beyond determination of magnitudes of mass emissions as has been common in the past, but also composition, size distribution, and size-distributed composition. Just as particles in the atmosphere are heterogeneous in these respects, so also are the sources. Considerable advance has been made recently these source properties, but it requires detailed, painstaking work. An outstanding example is the work of Cass and colleagues who have sampled a variety of combustion sources and presented size spectra and composition spectra (Kleeman et al., 1999) thereby demonstrating the feasibility of this approach. Measurements such as these together with inventories of activity may be expected to lead to a geographical source inventory for number and composition as a function of size.

A complementary approach that shows some real promise is characterization of source strengths of aerosols by micrometeorological methods that have been used in the past mainly for gases. Nemitz et al. (1999) conducted eddy correlation measurements at a single location in Edinburgh, Scotland, examining size dependent source strength of particles as a function of time, obtaining a spatial average flux as a function of upwind direction, Figure 15. The investigators call attention to the dependence of the source strength on wind direction, with a much lower flux when the wind direction is from the direction of a park and the suburbs than when it is from the city center and with a strong diurnal signal. It would appear that much more detailed map of emissions could be generated by an array of such measurements, albeit at considerable effort. Both this approach and the inventory approach based on activities are at an early stage of development, and it would seem that enhanced confidence would be gained by a combination of these approaches.

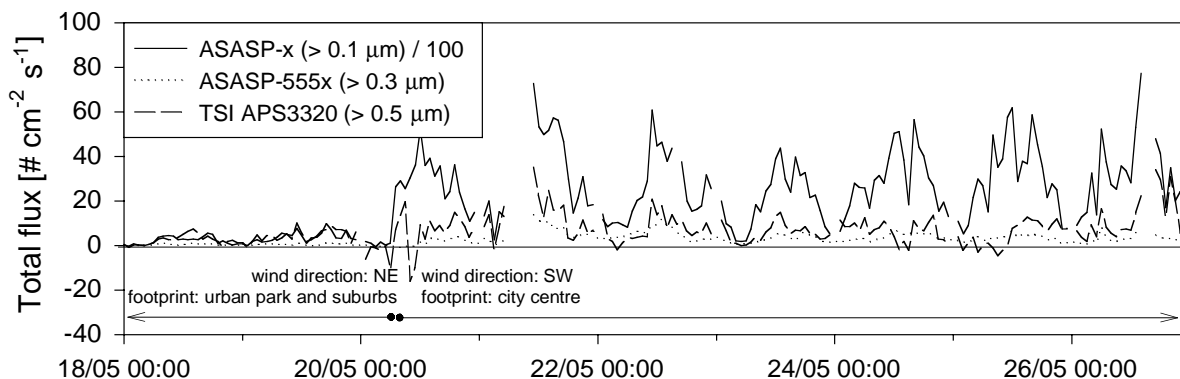


Figure 15. Time series of source number-flux of particles in three size ranges (optical diameter $> 0.1, \mu\text{m}$, $0.3 \mu\text{m}$, $0.5 \mu\text{m}$) measured in Edinburgh, Scotland in May, 1999. Negative flux denotes net deposition. (Nemitz et al., 2000).

MODELING TROPOSPHERIC AEROSOLS

At best measurements can provide information as to what is present at the location and time of the measurement. Satellite measurements can provide global coverage of aerosol loading such as (e.g., Figure 2) but with little detail of the properties. *In-situ* measurements can give a wealth of information on aerosol properties, but such measurements are inevitably sparse in space and time. Ultimately models are required to provide aerosol loading,

composition, and microphysical properties at locations and times where measurements are not made or cannot be made, to interpolate between and extrapolate beyond measurements and to provide necessary information for the past, and for the future for different emissions scenarios, devise control strategies.

What kind of models are required? Experience has shown that the only successful approach to this sort of modeling is by numerically simulating the governing processes based on mechanistic understanding. For aerosols such physical simulation models must accurately represent the key components of the aerosol life cycle: emissions of aerosols and precursors, chemical transformations responsible for gas-to-particle conversion, new particle formation, aerosol microphysical evolution, three-dimensional transport, and wet and dry removal processes of aerosols and precursors.

Inevitably the question arises as to the accuracy of models. For this reason the performance of models must be evaluated, by comparison with measurements, so the models certainly do not supplant measurements. But once the models have been evaluated over a wide range of conditions, they can be used with known confidence to evaluate aerosol loading and properties at present, for past times, and for future emissions scenarios. Such models then allow decision makers to examine alternative potential strategies and to select approaches that can meet the nation's needs effectively and efficiently.

Until the present time most aerosol models have focused on mass loading, often of one or a few constituents, rather than on microphysical properties. Work in our group has focused on sulfate, in part because of its importance as an aerosol constituent, and in part because the governing processes are sufficiently well understood to permit the modeling to be undertaken with some confidence. The model represents emissions of the several sulfur species, key gas- and aqueous-phase reactions, and removal by wet and dry deposition. The model tracks the several sulfur species and other key species. A distinguishing feature of this model is that it is driven by observationally-derived meteorological data. The variation in the governing meteorological variables, mainly wind velocities and precipitation, is responsible for the large temporal variability in modeled atmospheric constituents, as shown in Figure 16.

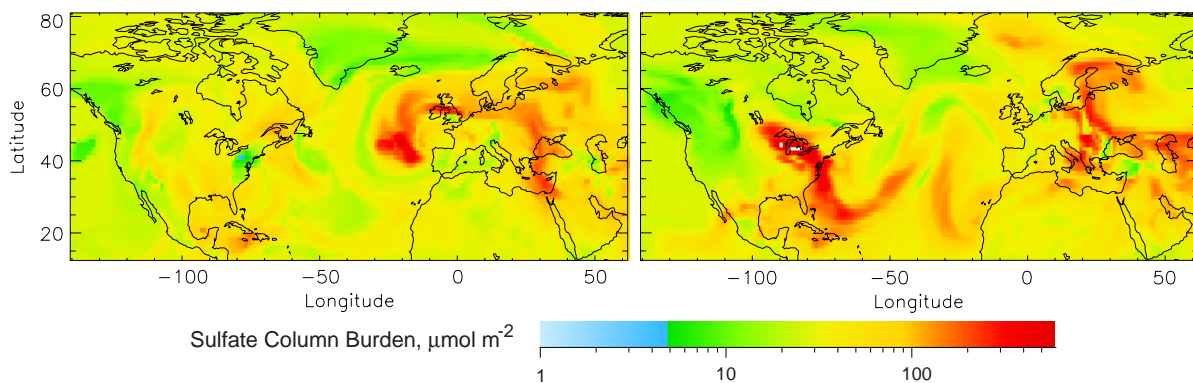


Figure 16. Modeled sulfate column burden (vertical integral of concentration) over the North Atlantic and adjacent continental regions at 1200 UTC on April 4 (left) and April 11, 1987, (right). Note the logarithmic scale covering two orders of magnitude. Based on calculations reported by Benkovitz and Schwartz (1997).

Model performance has been extensively evaluated (Benkovitz and Schwartz, 1997) by some 8000 model-observation comparisons for 24-hour sulfate and some 21000 comparisons for SO₂. To our knowledge this is the most extensive such comparison study of any model. For SO₂ the median ratio of modeled to observed concentrations was 0.97 and for sulfate 0.51. The underprediction of sulfate was tentatively attributed to lack of representation of transformations in nonprecipitating clouds. Much of the departure between modeled and observed MRs was attributed to subgrid spatial variation and nonrepresentative sampling of model grid cells at the stations used for the comparisons.

At the urban to regional scale pertinent models have been developed that represent multiple aerosol species and include representations of aerosol microphysics (*e.g.* Meng *et al.*, 1998). The latter is especially challenging because of the large number of variables that must be modeled to get accurate representation of the size distribution. Alternative approaches that are based on the moments of the aerosol size distribution look promising (Zhang *et al.*, 1999; Wright *et al.*, 2000). It is increasingly clear for the reasons outlined above that future models will need to represent aerosol microphysical processes governing their size and composition distributions.

ADDITIONAL OUTSTANDING ISSUES

The nucleation mechanism or mechanisms pertinent to new particle formation in the atmosphere are still not confidently understood. Much work has focused on binary nucleation of sulfuric acid and water, in part because of the presumed importance of this mechanism in the atmosphere and in part because sulfuric acid has been a testbed for nucleation studies in the laboratory and by theoreticians. However it is recently recognized that ternary nucleation involving ammonia can result in new particle formation at much lower concentration of sulfuric acid monomer than would be required for binary nucleation (Korhonen *et al.*, 1999), and there is evidence both of the occurrence of nucleation events in the atmosphere at such low sulfuric acid concentrations and of the possible role of NH₃ in such nucleation (Weber *et al.*, 1998).

Alternatively particles consisting mostly of sulfate may form without nucleation by growing on much smaller particles such as soot. As noted above, particles consisting mainly of sulfate often contain small soot inclusions, and many particles, even at rather high altitudes, which consist mainly of volatile material contain soot cores or, as shown in single particle mass spectrometry, nonvolatile minerals (Murphy *et al.*, 1998). As the mechanism of new particle formation plays a major role in the size distribution of aerosols the nucleation processes must be well understood before these dynamics can be modeled with confidence.

Understanding of the organic compounds in tropospheric aerosols remains sketchy. It is clear from Figure 1 that carbonaceous compounds can represent a major fraction of PM-2.5 mass, and the reported values may even be underestimates because of the presence of semivolatile organics that are lost in sampling. Key questions are: What are the organic compounds? To what extent are they primary versus secondary? To what extent do they derive from anthropogenic versus biogenic emissions? To what extent is the conversion of gaseous organic precursors to aerosol material enhanced by enhanced free radical concentrations associated with urban photochemical smog? A major impediment to answering these questions is capability for analysis of the organic component of aerosols. The frequent presentation of analytical results as "organic carbon" is more reminiscent of 19th century chemistry than of modern organic analysis, but in fairness, there are a myriad of compounds

present, all in small proportion. A number of groups have made substantial effort to analyze the organic fraction, and numerous compounds have been identified and in some cases related to sources, but even with modern gas-chromatography mass-spectrometric analysis only a quarter to at best half of the organic mass is elutable and detectable by gas chromatographic analysis (Mazurek *et al.*, 1997). Perhaps attention needs to focus on identifying the origin of the organic material by classes of compounds characteristic of different sources, with attention paid to compounds that can serve as markers for these classes. Likewise the incorporation of nitrates within the organic compounds may serve as a valuable tool in elucidating the involvement of photochemical oxidants in enhancing the conversion of gaseous precursors to organic aerosol.

DISCUSSION

The premise of this review is that aerosols possess many internal properties that must be accurately known, and for which the controlling processes must be understood, if effective and efficient control strategies are to be developed to control their atmospheric loading. Key among these properties are size distribution and size-dependent composition. These properties govern inhalation, light scattering, and activation to cloud droplets. Both size and composition are dynamic, evolving as gaseous substances (including, very importantly, water vapor) condense on, react in, and evaporate from the aerosol particles, as particles coagulate, and as particles are selectively removed from the atmosphere by dry deposition or by becoming activated into cloud drops and removed in precipitation. All of these processes are themselves dependent on the properties of the aerosol and therefore in turn on the sources of the aerosol and prior atmospheric processing.

The key driving force for standards for atmospheric aerosols is their association with impairment of human health. There is a large body of research adducing such an association, ranging from laboratory studies to field epidemiology and hospital admission rates. However the causative agent or agents remain unknown: Are adverse health effects due simply to mass loading, or are they associated with specific aerosol constituents or properties? If specific health influencing agents can be identified, it may be possible to zero in on controlling the concentrations of these species. The result will be both better health for exposed populations and a more efficient strategy of achieving this than simply wholesale reduction of PM-2.5 concentrations. Developing the understanding that will allow both the identification of specific health influencing agents, if any, and developing effective control strategies, either for PM-2.5 or for specific aerosol components, will be a challenging task.

A key component of developing and demonstrating the requisite understanding is representing this understanding in models and evaluating that understanding by comparison of model results with observations. Accurate description of aerosol dynamics requires understanding of the controlling physics and chemistry and knowledge of pertinent input variables, together with much more demanding computational capabilities than for representation of chemical processes. All of these are lacking to some extent, but are being actively pursued.

CONCLUSIONS

It is no longer appropriate, if it ever was, to think of atmospheric aerosols as homogeneous spheres of uniform composition and size. Within the United States, and even more globally, not only the mass loading but also the composition, morphology, and size distribution of atmospheric aerosols are highly variable, as a function of location, and at a given location as a function of time. Particles of a given aerodynamic size may differ from one another, and even within individual particles material may be inhomogeneously distributed, as for example, carbon spherules imbedded in much larger sulfate particles. Some of the particulate matter is primary, that is, introduced into the atmosphere directly as particles, such as carbon particles in diesel exhaust. Some is secondary, that is, formed in the atmosphere by gas-to-particle conversion. Much of the material is inorganic, mainly sulfates and nitrates resulting mainly from energy-related emissions. Some of the material is carbonaceous, in part primary, in part secondary, and of this material some is anthropogenic and some biogenic.

While the heterogeneity of atmospheric aerosols complicates the problem of understanding their loading and distribution, it may well be the key to its solution. By detailed examination of the materials comprising aerosols it is possible to infer the sources of these materials. It may be possible as well to identify specific health impairing agents. The heterogeneity of aerosol particles is thus the key to identifying their sources, to understanding the processes that govern their loading and properties, and to devising control strategies that are both effective and efficient. Future research must therefore take cognizance of differences among aerosol particles and use these differences to advantage.

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REFERENCES

- Benkovitz C. M. and Schwartz S. E. Evaluation of Modeled Sulfate and SO₂ over North America and Europe for Four Seasonal Months in 1986-87. *J. Geophys. Res.* **102**, 25305-25338 (1997).
- Buseck P. and Pósfai M. Airborne minerals and related aerosol particles: Effects on climate and the environment. *Proc. Nat. Acad. Sci. USA* **96**, 3372-3379 (1999).
- EPA (Environmental Protection Agency). National Air Quality and Emissions Trends Report, 1997 Report 454/R-98-016. Office of Air Quality Planning and Standards Emissions Monitoring and Analysis Division; Air Quality Trends Analysis Group. Research Triangle Park, NC 27711 December 1998; <http://www.epa.gov/oar/aqtrnd97/index.html>.
- Haywood J. M., Ramaswamy V., and Soden B. J. Tropospheric Aerosol Climate Forcing in Clear-Sky Satellite Observations over the Oceans. *Science* **283**, 299-1303 (1999).
- Holben, B. N. *et al.* AERONET -- A federated instrument network and data archive for aerosol characterization, *Remote Sens. Environ.* **66**, 1-16 (1998); <http://aeronet.gsfc.nasa.gov:8080/>.
- Hughes L. S. *et al.* The size and composition distribution of atmospheric particles in Southern California, *Environ. Sci. Technol.* **33**, 3506--3515 (1999).

- Husar R. B. and Falke S. R. The Relationship Between Aerosol Light Scattering and Fine Mass (1996) <http://capita.wustl.edu/CAPITA/CapitaReports/BScatFMRelation/BSCATFM.HTML>.
- Kleeman M. I., Schauer J. J. and Cass G. R. Size and composition distribution of fine particulate matter emitted from wood burning, meat charbroiling, and cigarettes. *Environ. Sci. Technol.* **33**, 3516-3523 (1999).
- Korhonen P., M. Kulmala, A. Laaksonen, Y. Viisanen, R. McGraw, and J. H. Seinfeld, Ternary nucleation of H₂SO₄, NH₃, and H₂O in the atmosphere, *J. Geophys. Res.* **104**, 26349-26353 (1999).
- IPCC (Intergovernmental Panel on Climate Change). *Climate Change 1995 - The Science of Climate Change*. Editors: J T Houghton *et al.* (Cambridge University Press, Cambridge U.K., 1996).
- JPL (Jet Propulsion Laboratory) LITE (Lidar In-space Technology Experiment) Science <http://www-a.jpl.nasa.gov/lidar/lite.htm>.
- Mazurek, M. *et al.* Visibility-reducing organic aerosols in the vicinity of Grand Canyon National Park: Properties observed by high-resolution gas-chromatography. *J. Geophys. Res.* **102**, 3779-3793 (1997).
- Meng, Z. D. Dabdub, and J. H. Seinfeld, Size-resolved and chemically resolved model of atmospheric aerosol dynamics, *J. Geophys. Res.*, **103**, 3419-3435, 1998.
- Murphy D. M., D. S. Thomson, and M. J. Mahoney. In Situ Measurements of Organics, Meteoritic Material, Mercury, and Other Elements in Aerosols at 5 to 19 Kilometers. *Science* **282**, 1664-1669 (1998).
- Nakajima T., Higurashi A., Takeuchi N., and Herman J. R. Satellite and ground-based study of optical properties of 1997 Indonesian forest fire aerosols. *Geophys. Res. Lett.* **26**, 2421-2124 (1999).
- NASA (National Aeronautics and Space Administration). Pathfinder Instruments for Cloud and Aerosol Spaceborne Observations/Climatologie Etendue des Nuages et des Aerosols (PICASSO-CENA) <http://essp.gsfc.nasa.gov/picasso-cena.html>.
- Nemitz E., Theobald M. R., McDonald A. D., Fowler D., Dorsey J., Bower K. and Gallagher M. W. Direct micrometeorological eddy-correlation measurements of size-dependent particle emission above a city. In: Proceedings of EUROTRAC Symposium 2000. (WITpress, Southampton U.K., 2000), in press.
- Richardson, B. Remarks by Secretary of Energy Bill Richardson, Conference on Air Quality, Washington, DC, Dec. 1, 1998. <http://www.doe.gov/news/speeches98/decss/airquality.htm>.
- Rosenfeld D. Suppression of rain and snow by urban and industrial air pollution. *Science* **287**, 1793-1796 (2000).
- Strawbridge K.A., and Hoff R.M. LITE Validation Experiment Along California's Coast: Preliminary Results. *Geophys. Res. Lett.* **23**, 73- 76 (1996).
- Tang, I. N., Chemical and size effects of hygroscopic aerosols on light scattering coefficients, *J. Geophys. Res.* **101**, 19245-19250 (1996).
- Weber, R. J. *et al.* A study of new particle formation and growth involving biogenic and trace gas species measured during ACE-1. *J. Geophys. Res.* **103**, 16385-16396 (1998).
- Zhang X. Q., McMurry P. H., Hering S. V., and Casuccio G. S. Mixing characteristics and water content of submicron aerosols measured in Los Angeles and at the Grand Canyon. *Atmos. Environ.* **27A** 1593-1607 (1993).
- Zhang, Y., C. Seigneur, J. H. Seinfeld, M. Z. Jacobson, and F. S. Binkowski, Simulation of Aerosol Dynamics: A Comparative Review of Algorithms Used in Air Quality Models, *Aerosol Science and Technology*, 31, 487-514 (1999).
- Wright D. L., McGraw R., Benkovitz C. M., and Schwartz S. E. Six-moment representation of multiple aerosol populations in a sub-hemispheric chemical transformation model. *Geophys Res. Lett.* **27**, 967-970 (2000).